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TestAmerica, Inc.

Dayton Division



## Standard Operating Procedure

Analyte or Suite: ICP Aqueous Sample Preparation

Methodology: Acid Digestion Procedure for ICP

Reference: Method 3010A, SW-846, 3rd Edition

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## 1. INTRODUCTION AND SCOPE

### 1.1. General

Preservation: HNO<sub>3</sub> to pH <2, Cool - 40 C

Container: 500cc plastic, glass is also acceptable

Minimum sample volume: 50 mL for a single digestion

Holding Time: 6 months

Method No.(s) and References:

3010, SW-846, 3rd Edition

Metals, Section 4.1.3., EPA 600/4-79-020, Revised March 1983

1.2. This method is an acid digestion procedure used to prepare aqueous samples, TCLP, EPTOX, and mobility-procedure extracts, and wastes that contain suspended solids for the analysis by flame atomic absorption spectroscopy or by inductively coupled plasma spectroscopy.

1.3. Samples prepared by this method may be analyzed by ICP for the following metals:

Aluminum	Chromium	Potassium
Arsenic	Cobalt	Selenium
Barium	Copper	Sodium
Beryllium	Iron	Thallium
Cadmium	Lead	Vanadium
Calcium	Magnesium	Zinc
	Manganese	
	Molybdenum	Antimony
	Nickel	Silver

It is possible to use this method as a preparation procedure for other elements not specifically listed. If this is the case, the Quality Control Indicators (QCI) should be closely evaluated to determine this method's applicability. Refer to Section 11. Summary of Modifications/Method Comparision for additional discussion.

1.4. Your ability to follow this method according to the specifications herein will affect your performance evaluations, the quality of data produced for this application, your section's productivity, and the laboratory's profitability.

## 2. SUMMARY OF METHOD

A mixture of HNO<sub>3</sub> and the material to be analyzed is refluxed in a Griffin beaker until the digestate is light in color or until its color has stabilized. After the digestate has been brought to a low volume, it is refluxed with HCl and brought up to volume. If sample should go to dryness, it must be discarded and the sample reprepared.

## 3. SAFETY

Each employee is directly responsible for complete awareness of all health hazards associated with every chemical that he/she uses. The employee must be aware of these hazards, and all associated protective wear and spill clean-up procedures PRIOR TO THE USE of any chemical. In all cases, both the applicable MSDS and supervisor or Safety Officer should be consulted. The employee should comply with all safety policies as presented in the TestAmerica Safety Manual. The bottle labels also provide important information that must be noted. Personnel performing this procedure may be working with flammables, poisons, toxics, carcinogens, teratogens, mutagens, and biohazards. In particular, approved gloves, safety glasses, and labcoats must be worn, and solvents will be handled in ventilated hoods, in addition to other measures prescribed by the Division. It should be noted that samples must be handled with as much care as any of the materials used in this method due to the unknown nature of their composition.

## 4. REAGENTS AND MATERIALS

### 4.1. Apparatus.

#### 4.1.1. Hot Plate

4.1.2. 150 mL beakers, VWR Catalogue No. 13912-182 or other appropriate vessels such as erlenmeyer flasks.

#### 4.2. Reagents.

All reagents must be properly labelled with the reagent identification and concentration, date prepared, expiration date, initials of analyst, and applicable safety information. Labels are available through the centralized purchasing system. The label has a place for the NFPA diamond, which will be used to indicate health (blue), flammability (red), reactivity (yellow), and contact/special (white) information obtained from applicable Material Safety Data Sheets (MSDS) supplied by the vendor.

4.2.1. Deionized water: Prepare by passing water through a mixed bed of cation and anion exchange resins or an equivalent source. Use deionized water for the preparation of all reagents, standards, and dilution water.

4.2.2. Concentrated Nitric Acid, VWR Catalogue No. JT9601-33. If metal impurities are found to be present, use a spectrograde acid.

HNO<sub>3</sub>

NFPA diamond: health = 3, flammability = 0, reactivity = 3, contact = 4.

Strong oxidizer. Contact with other material may cause fire. Liquid and vapor cause severe burns. May be fatal if swallowed. Harmful if inhaled and may cause delayed lung injury. Keep from contact with clothing and other combustible materials. Do not get in eyes, on skin.

4.2.3. Concentrated Hydrochloric Acid, VWR Catalogue No. JT9535-33. If metal impurities are found to be present, use a spectrograde acid.

HCl

NFPA diamond: health = 3, flammability = 0, reactivity = 2, contact = 3.

Poison! Danger! Causes severe burns. May be fatal if swallowed. Do not get in eyes, on skin, on clothing. Avoid breathing vapor. Keep in tightly closed container. use with adequate ventilation. Wash thoroughly after handling.

4.2.4. Hydrochloric Acid (1:1): prepare a 1:1 dilution with deionized water by adding the concentrated acid to an equal volume of water.

#### 4.3. Standards.

See the appropriate analytical SOP for details.

## 5. INTERFERENCES

5.1. Interferences are discussed in the analytical SOPs.

## 6. ANALYTICAL PROCEDURES

### 6.1. Preservation and Handling.

6.1.1. For the determination of acid-soluble metals, contamination and loss are of prime concern. Dust in the laboratory environment, impurities in reagents and improperly cleaned laboratory apparatus which the sample contacts are all potential sources of contamination. Sample containers can introduce either positive or negative errors in the measurement of metals by (a) contributing contaminants through leaching or surface desorption and/or (b) by depleting concentration through adsorption, thus the collection and treatment of the sample prior to analysis requires particular attention. The quality control program should document through the use of spiked samples, reagent and sample blanks, that cleaning procedures are adequate. Before collection of the sample a decision must be made as to the type of data desired, ie., dissolved, suspended, or total.

6.1.2. All metals samples (except Cr VI) must be acidified to a pH < 2 with nitric acid upon collection, except samples which need to be filtered at the laboratory. Ideally, samples requiring filtration should be filtered in the field. Mercury analyses must be conducted within 28 days; other metals analyses have a holding time of six months.

6.1.3. For the determination of dissolved constituents the sample must be filtered through a 0.45 u membrane filter as soon as practical after collection. A glass fiber pre-filter may be used in combination with the 0.45 u membrane filter. Glass or plastic filtering apparatus using membrane filters are recommended to avoid possible contamination. Use the first 50-100 ml to rinse the filter flask. Discard this portion and collect the required volume of filtrate. Acidify the filtrate with 1:1 HNO<sub>3</sub> to a pH of <2. Normally, 2-3 ml of (1:1) acid per liter should be sufficient to preserve the sample. Analyses performed on a sample so treated shall be reported as "dissolved" concentrations.

### 6.2. Glassware Preparation.

6.2.1. All glassware for metals analysis will be kept separate and labelled for metal analysis only.

### 6.3. Sample Analysis.

6.3.1. Transfer a 50 to 100-mL representative aliquot of well mixed sample to a 150-mL Griffin beaker. Choose a volume of sample appropriate for the expected concentration of metals. The sample volume required may vary proportionally with the number of metals to be determined. Add 3 mL of concentrated  $\text{HNO}_3$ . Place the beaker on a hot plate and cautiously evaporate to the lowest reasonable volume, making certain that the sample does not boil and that no portion of the bottom of the beaker is allowed to go dry. Cool the beaker.

Note: If a sample is allowed to go to dryness, low recoveries will result. Should this occur, discard the sample and reprepare.

6.3.2. If necessary, continue heating, adding additional acid until the digestion is complete. Generally, this is indicated when the digestate is light in color or does not change in appearance with continued refluxing and evaporate to a low volume. Add a small quantity of 1:1  $\text{HCl}$  (5 mL/50 mL of final solution) and warm the beaker for an additional 15 minutes to dissolve any precipitate or residue resulting from evaporation.

6.3.3. Wash down the beaker walls with deionized water and bring to 5 mL volume in a volumetric flask. The sample is now ready for analysis.

### 6.4. Calculation.

6.4.1. The concentrations determined in the digest are to be reported based on the following calculation:

$$\text{Concentration mg/L} = \frac{C \times V_f}{V_i}$$

where: C = Instrument readout, (mg/L)  
Vf = Final volume (mL) of digested sample  
Vi = Initial volume (mL) of sample

Additional dilutions made at the time of analysis should also be included in the calculation.

## 7. Quality Control.

### 7.1. Method Performance.

#### 7.1.1. Calibration Curve.

Not Applicable

#### 7.1.2. Initial Calibration Verification Standard (ICVS).

Not Applicable

#### 7.1.3. Reagent Blank (RB).

Not Applicable

#### 7.1.4. Continuing Calibration Verification Standard (CCVS).

Not Applicable

#### 7.1.5. Procedure Blank (PB).

The procedure blank is a deionized water blank that is subjected to the same conditions that a prepared sample undergoes. Preparation includes digestion. Analyze a minimum of one procedure blank per batch. A batch shall contain twenty samples or less. Interim acceptance criteria requires the procedure blank to be less than the reporting limit. Statistical warning limits require the procedure blank to be within  $\pm$  two standard deviations of the mean from a data base of 20 points. Statistical control limits require the blank to be less than the reporting limit. Procedure blanks are not routinely subtracted from the analytical results. Enter the procedure blank result into LABSYS II.

NOTE: If you have performed a dilution on the sample and need to assess the procedure blank, be sure to evaluate the result obtained from the analysis of the procedure blank at the same dilution.

#### 7.1.6. Lab Control Standard (LCS).

The lab control standard is a high standard that is subjected to the same conditions that a prepared sample undergoes. Preparation includes digestion. Analyze a minimum of one LCS per batch. A batch shall contain twenty samples or less. Interim acceptance criteria requires the LCS to be within 80-120% of the true value. Statistical acceptance criteria require the LCS to be within  $\pm$  three standard deviations of the mean from a data



base of 20 points. Enter the LCS result into LABSYS II.

#### 7.1.7. Matrix Spike / Matrix Spike Duplicate (MS/MSD).

The matrix spike / matrix spike duplicate pair are two separate aliquots of sample which are spiked with known concentrations of analyte and subjected to the same conditions that a sample undergoes. The spike concentration should be 20% of the top standard or equal the CLP spike guidelines. Analyze a minimum of one MS/MSD pair per every analytical batch per matrix; the two matrices monitored are water and other ie. soils and other solids and an analytical batch is twenty samples or less. Advisory interim acceptance criteria requires the MS/MSD percent recovery to be within 75-125% and the relative percent difference to be less than 20. Advisory statistical warning limits require the MS/MSD percent recovery and RPD to be within  $\pm$  two standard deviations of the mean from a data base of 20 points. Advisory statistical control limits require the MS/MSD percent recovery and RPD to be within  $\pm$  three standard deviations of the mean from a data base of 20 points. The data generated can be presented, if necessary, as a statement of precision and accuracy for a particular analysis on a given matrix. Enter the MS/MSD results into LABSYS II.

#### 7.2. Corrective Action.

If any of the method performance criteria outlined above cannot be met, notify your supervisor immediately.

#### 7.3. Documentation.

All quality control data should be maintained and available for easy reference and inspection.

#### 7.4. Analyst Certification.

##### 7.4.1. Initial Certification.

Each analyst performing this method must successfully complete PE samples, which are administered by the QC Coordinator.

##### 7.4.2. Continued Certification.

Each analyst performing this method must successfully complete at least 1 ITP sample during a 12 month period.

#### 7.5. Method Detection Limits and Reporting Limits.

Not Applicable

## 8. REFERENCES

8.1. Methods for Chemical Analysis of Water and Wastes, USEPA, Environmental Monitoring and Support Laboratory EPA-600/4-79-020

8.2. Standard Methods For the Examination of Water and Wastewater, 17th Edition, APHA

8.4. Annual Book of ASTM Standards, Part 31, "Water," Standard D 2574-79, p. 469 (1976)

## 9.0 DAILY ANALYTICAL SEQUENCE

1. Procedure Blank (PB): < Reporting Limit, 1 per batch - a batch shall be 20 samples or less.
2. Lab Control Standard (LCS): 80-120% of the true value or within the statistically established range, 1 per batch - a batch shall be 20 samples or less.
3. Matrix Spike/Matrix Spike Duplicate (MS/MSD): 1 per batch - a batch shall be 20 samples or less.
4. Samples 1 - 20
5. Return to #1 if additional samples will be processed.

## 10. TIPS AND HINTS

It is important that feedback of QC analytical results be provided by the analytical team to the digestion team.

### Dayton Division Specific Appendix

Item: 1.3. Samples prepared for this method may be analyzed by FLAAS or ICP for the following metals:

In addition to the metals listed in the SOP the following may be analyzed by ICP: Li, Sr, Si, Sn, Ti.

Item: 4.1.2. 150 mL beakers...

100 or 150 mL beakers are used. Fisher Cat.# 02-540H/02-540J

Item: 4.2.2. Concentrated Nitric Acid...

Ultra-pure grade concentrated nitric acid is used - Fisher A 509-212.

Item: 6.2.2. After washing, all glassware...

The Dayton specific glassware washing procedure has been presented in the following.

#### BEAKERS AND WATCHGLASS COVERS

1. Wash with soft cloth and hot, water.
2. Wash in dishwasher.
3. Bake until dry.

#### GRADUATED CYLINDERS AND FILTERING APPARATUS

1. Rinse with 1% nitric acid (minimum of 3 times).
2. Rinse with DI (minimum of 3 times).

#### VOLUMETRIC FLASKS

Between uses:

1. Rinse with 1% nitric acid (minimum of 3 times).
2. Rinse with DI (minimum of 3 times).

End of Day:

All volumetric flasks will be soaked overnight with 1% nitric acid.

Note: Volumetric flasks will be soaked over the weekend in 1:1 nitric acid then followed by steps 1 and 2 above.

Item: 6.3. Sample Analysis. (6.3.1. - 6.3.3.)

A 50 mL volume of a well-mixed sample is digested by placing the sample volume plus 3.0 mL of concentrated nitric acid in a beaker. Place the beaker on a hot plate, evaporate to app. 20-25 mls, then allow the beaker to cool. If particulates are still at a high level, additional concentrated nitric acid is added and the sample is heated further. (NOTE: Do not add more

than 7.5mL of nitric acid total. If further additions of nitric acid are indicated, the digestion procedure should be repeated using a smaller sample aliquot.)

When the sample has completely digested, evaporate to app. 20 mls, add 5 mL of 1:1 hydrochloric acid and warm the sample 10-15 min. Transfer the sample to a volumetric flask, wash down the beaker and bring the sample to the final volume of 50 mL with deionized water. A general indication that digestion is complete is when the digestate is light in color or there is no further change in the appearance.

**Item: 7.1.6. Lab Control Standard (LCS)**

The following are the premixed standards used to make the QC standards. They are purchased from Fisher Chemical Supply.

**QC-7 Spex Catalog #QC-7-500**

Al	100 mg/L	Si	500 mg/L
Ba	100 mg/L	Ag	100 mg/L
B	100 mg/L	Na	100 mg/L
K	1000 mg/L		

**QC-19 Spex Catalog QC-19-500**

Sb	100 mg/L	Mg	100 mg/L
As	100 mg/L	Mn	100 mg/L
Be	100 mg/L	Mo	100 mg/L
Cd	100 mg/L	Ni	100 mg/L
Ca	100 mg/L	Se	100 mg/L
Cr	100 mg/L	Tl	100 mg/L
Co	100 mg/L	Ti	100 mg/L
Cu	100 mg/L	V	100 mg/L
Fe	100 mg/L	Zn	100 mg/L
Pb	100 mg/L		

**MN-4 Spex Catalog #MN-4-500**

Ca	500 mg/L	K	100 mg/L
Mg	100 mg/L	Na	500 mg/L

The spiking solutions consist of three purchased solutions and one made from 1000 ppm stock.

The three purchased solutions are:

- QC-7 SPEX catalog # QC-7-500
- QC-19 SPEX catalog # QC-19-500
- MN-4 SPEX catalog # MN-4-500

Multi-element Spiking Solution

The multi-element spiking solution (M.E. Spike) prepared from 1000 ppm stock is made by:

<u>Volume</u>	<u>Conc.</u>	<u>Diluted to with 5% HNO3</u>
10 ml	1000 ppm Si	100 ml
10 ml	1000 ppm Sr	
10 ml	1000 ppm Sn	

Digested Standards

<u>Volume</u>	<u>Conc.</u>	<u>Added to</u>
0.5 ml	QC-7	
0.5 ml	QC-19	50 ml deionized water
2.0 ml	MN-4	or sample
2.0 ml	ME Spike	

Spiking Solution Concentrations

<u>Element</u>	<u>Digested LCS, MS, MSD</u>
Al	1.00
Sb	1.00
As	1.00
Ba	1.00
Be	1.00
B	1.00
Ca	21.0
Cd	1.00
Cr	1.00
Co	1.00
Cu	1.00
Fe	1.00
Pb	1.00
Mg	5.0
Mn	1.00
Mo	1.00
Ni	1.00
K	14.0
Se	1.00
Si	4.5
Ag	1.00
Na	21.0
Sr	4.00
Tl	1.00
Sn	4.0
Ti	1.00
V	1.00
Zn	1.00

#### SHELF LIFE OF CALIBRATION AND SPIKING STANDARDS

##### 1000 ppm Standards

6 Months from date of opening  
1 year from receipt unopened  
expiration date on bottle from manufacturer

##### Stock Solutions

Flame 1 Month  
ICP 3 Months

##### Working Standards

Flame 1 Month  
ICP 1 Month

##### Spiking Solutions

1 month from date of preparation if not  
purchased; if spiking solution is purchased  
1 year from date of opening or expiration  
date on bottle (earliest date).

#### Item: 7.1.7. Matrix Spike/Matrix Spike Duplicate (MS/MSD)

The MS/MSD spiking solutions are the same as the LCS spiking solutions see 7.1.6.

#### Item: 7.3. Documentation

##### Verification of Data

All analytical data will be verified for completeness of QCI requirements, and will be spot checked for correct calculations. This verification will be performed by a competent analyst or the area supervisor.

After an analyst completes training on a parameter, passes a PE analysis, and demonstrates good data production for 90 days, he/she will be permitted to perform self verification of data using the form labeled as Attachment 1.

Specific documentation that needs to be completed:

Area to Document	Frequency	Acceptance Criteria
Standard/Reagent Log Book	upon opening bottle whenever a spk soln. is made	NA NA
Auto pipette	monthly	±4% by wt. on balance

Item: 7.4.1. Initial Certification.

Currently no self test is available.

Item: 10. Tips and Hints.

#### METALS PREPARATION CHECK LIST

##### DAILY

1. Empty water bottles - refill at beginning of day.
2. Empty Ultra-pure HNO<sub>3</sub> - refill at beginning of day.
3. Empty 1:1 HCl - refill at beginning of day.
4. Pull hood doors down, turn exhaust fans off, turn light off, and check that all hot plates are turned off or unplugged.
5. Place dirty glassware in glass cleaning area.
6. Fill dilution volumetric flasks with 1% for soaking over night. Soak with 1:1 HNO<sub>3</sub> over weekends.
7. Check the expiration dates of spiking solutions and remake when dates indicate.
8. Put the samples on the shelves that have already been set up.
9. Clean out hoods as needed.

##### WEEKLY

1. Replace paper on counters.